

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE (REV. 11-2000)		ATTORNEY'S DOCKET NUMBER 1082-033
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		
INTERNATIONAL APPLICATION NO. PCT/US99/24013	INTERNATIONAL FILING DATE 09 November 1999	PRIORITY DATE CLAIMED 12 November 1998
TITLE OF INVENTION Method for the Synthesis of Energetic Thermoplastic Elastomers In Non-Halogenated Solvents		
APPLICANT(S) FOR DO/EO/US Andrew J. Sanderson; Wayne W. Edwards		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
<ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). <input type="checkbox"/> has been communicated by the International Bureau. <input checked="" type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> <input type="checkbox"/> is attached hereto. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). <input type="checkbox"/> have been communicated by the International Bureau. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <input checked="" type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 		
Items 11 to 20 below concern document(s) or information included: <ol style="list-style-type: none"> <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. <input checked="" type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). <input checked="" type="checkbox"/> Other items or information: Power of Attorney forms Demand, Request, IPER 		

U.S. APPLICATION NO (if known, see 37 CFR 1.492(e)) 09/851411	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER																																														
<p>21. <input checked="" type="checkbox"/> The following fees are submitted:</p> <p>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</p> <p>Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00</p> <p>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00</p> <p>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00</p> <p>International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00</p> <p>International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00</p> <p style="text-align: center;">ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 860.00</p> <p>Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)). \$</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 15%;">CLAIMS</th> <th style="width: 25%;">NUMBER FILED</th> <th style="width: 25%;">NUMBER EXTRA</th> <th style="width: 25%;">RATE</th> <th style="width: 10%;">\$</th> </tr> </thead> <tbody> <tr> <td>Total claims</td> <td>33 - 20 =</td> <td>13</td> <td>x \$18.00</td> <td>\$ 234.00</td> </tr> <tr> <td>Independent claims</td> <td>2 - 3 =</td> <td>0</td> <td>x \$80.00</td> <td>\$</td> </tr> <tr> <td colspan="2">MULTIPLE DEPENDENT CLAIM(S) (if applicable)</td> <td>0</td> <td>+ \$270.00</td> <td>\$</td> </tr> <tr> <td colspan="4" style="text-align: right;">TOTAL OF ABOVE CALCULATIONS =</td> <td>\$ 1094.00</td> </tr> </tbody> </table> <p><input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. \$</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th colspan="2" style="width: 80%;">SUBTOTAL =</th> <th style="width: 20%;">\$ 1094.00</th> </tr> </thead> <tbody> <tr> <td colspan="3">Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). \$</td> </tr> <tr> <td colspan="2" style="text-align: right;">TOTAL NATIONAL FEE =</td> <td>\$ 1094.00</td> </tr> <tr> <td colspan="2">Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +</td> <td>\$ 40.00</td> </tr> <tr> <td colspan="2" style="text-align: right;">TOTAL FEES ENCLOSED =</td> <td>\$ 1134.00</td> </tr> <tr> <td colspan="2"></td> <td style="text-align: right;">Amount to be refunded: \$</td> </tr> <tr> <td colspan="2"></td> <td style="text-align: right;">charged: \$</td> </tr> </tbody> </table>		CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	Total claims	33 - 20 =	13	x \$18.00	\$ 234.00	Independent claims	2 - 3 =	0	x \$80.00	\$	MULTIPLE DEPENDENT CLAIM(S) (if applicable)		0	+ \$270.00	\$	TOTAL OF ABOVE CALCULATIONS =				\$ 1094.00	SUBTOTAL =		\$ 1094.00	Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). \$			TOTAL NATIONAL FEE =		\$ 1094.00	Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +		\$ 40.00	TOTAL FEES ENCLOSED =		\$ 1134.00			Amount to be refunded: \$			charged: \$	<p>CALCULATIONS PTO USE ONLY</p>
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<p>a. <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed.</p> <p>b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>501324</u> in the amount of \$ <u>1134.00</u> to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>501324</u>. A duplicate copy of this sheet is enclosed.</p> <p>d. <input type="checkbox"/> Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.</p>		 SIGNATURE <u>David S. Taylor</u> <u>May 7, 2001</u> NAME <u>39,045</u> REGISTRATION NUMBER																																														
<small>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.</small>																																																
<small>SEND ALL CORRESPONDENCE TO:</small>																																																
<small>Sullivan Law Group 5060 North 40th Street Suite 120 Phoenix, AZ 85018 (602) 956 6161 (phone) (602) 956 6262 (fax)</small>																																																

09/831411

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

In re Patent Application of

Docket: 1082-033

SANDERSON et al.

Application No.: Not Yet Assigned

Filed: Herewith

Title: METHOD FOR THE SYNTHESIS
OF ENERGETIC THERMOPLASTIC
ELASTOMERS IN NON-HALOGENATED SOLVENTS

* * *

May 7, 2001

PRELIMINARY AMENDMENT

Hon. Commissioner of Patents
And Trademarks
Washington, D.C. 20231

Dear Sir:

Kindly preliminarily amend the above-identified application as indicated in the attached sheets.

IN THE ABSTRACT:

Kindly replace the original abstract with the attachment.

IN THE SPECIFICATION:

Kindly amend the specification by inserting on page 1, before line 1, the paragraph set forth on the attached sheet.

IN THE CLAIMS:

Kindly amended claims 1-4, 19-22, and 30-33 as set forth on the attached sheets.

REMARKS

Claims 1-33 remain pending in this application.

A substitute abstract has been submitted herewith to limit the word count to 150 words or less. The substitute abstract is supported by the original disclosure, such that no new matter would be introduced by entry thereof. Accordingly, approval and entry are respectfully requested.

The specification has been amended herein to include reference to the priority PCT International Application. Applicants point out that a Rule 34 Amendment was made during prosecution of the PCT International Application to include reference to the priority provisional application. The Examiner's attention is directed to the substituted sheet of the International Preliminary Examination Report.

Applicants respectfully submit that the amendments to the claims are fully supported by the original disclosure, and that no new matter would be introduced by entry thereof. Specifically, the amendments to claims 1-4, 19-22, and 30-33 have been presented to clarify Applicants' invention further.

Accordingly, approval and entry of the attached claim amendments are respectfully requested.

The claims, as presented herein, are submitted to be in condition for allowance and an early Notice to that effect is requested.

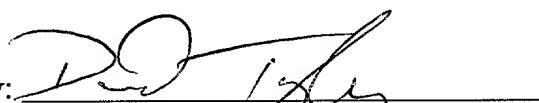
If, after reviewing the above, the Examiner believes any issues remain unresolved, the favor of an Examiner interview is requested and the Examiner is requested to contact the undersigned, by telephone, to schedule same.

It is Applicants' understanding that there is no fee due in connection with the filing of this Preliminary Amendment. If there are any other fees due in connection with the filing of this application or otherwise relating to this application, please charge the fees to our Deposit Account No. 501324, under Order No. 1082-033.

Respectfully submitted,

Sullivan Law Group

By:



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STS/DST

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ABSTRACT OF THE DISCLOSURE

A method is provided for preparing thermoplastic elastomers. A blocks of the thermoplastic elastomers are crystalline at temperatures below about 60°C and are derived from oxetane derivatives and/or tetrahydrofuran derivatives. B blocks of the thermoplastic elastomer are amorphous above about -20°C and are derived from oxetanes, tetrahydrofuran, oxiranes, and derivatives thereof. According to this method, the A and B blocks are dissolved into solution containing a non-halogenated solvent, preferably tetrahydrofuran, then dried by azeotropic distillation. The dried blocks are end-capped with a diisocyanate, preferably a diisocyanate having one isocyanate moiety substantially more reactive with the terminal groups of the blocks than the other isocyanate moiety of the diisocyanate. The end-capped blocks are then linked together with a linking compound.

SPECIFICATION:

Insert on page 1, before line 1, the following:

--This is a national stage application under 37 U.S.C. § 371 of
PCT/US99/24013 filed on November 9, 1999.--

AMENDED CLAIMS:

1. (Once amended) A method of preparing a thermoplastic elastomer [having A blocks which are crystalline at temperatures blow about 75°C and the B blocks which are amorphous at temperatures above about -20°C, the method] comprising:

(a) dissolving [the] A blocks and B blocks terminated with respective isocyanate-reactive groups at approximately [the] stoichiometric ratios [that are] intended to be present in the thermoplastic elastomer into solution comprising at least one non-halogenated solvent, the A blocks being crystalline [at temperatures] below about 75°C and derived from monomers comprising at least one member selected from the group consisting of oxetane derivatives and tetrahydrofuran derivatives, the B blocks being amorphous [at temperatures] above about -20°C and derived from monomers comprising at least one member selected from the group consisting of oxetane and derivatives thereof, tetrahydrofuran and derivatives thereof, and oxirane and derivatives thereof;

(b) drying the dissolved A blocks and B blocks of water by azeotropic distillation of the non-halogenated solvent;

(c) end-capping the dried A blocks and the dried B blocks in the non-halogenated solvent by reacting the dried A blocks and the dried B blocks with at least one diisocyanate in which a first isocyanate moiety thereof is substantially more reactive with the terminal groups of the blocks as a second isocyanate moiety thereof, whereby the more reactive first isocyanate moiety is capable of reacting with the terminal groups of the blocks, leaving the less reactive second isocyanate moiety free and unreacted; and

(d) linking the end-capped A blocks and the end-capped B blocks together in the non-halogenated solvent with at least one linking compound comprising two isocyanate-reactive groups which are sufficiently sterically

unhindered to react with the free and unreacted isocyanate moieties of the end-capped [polymers] blocks.

2. (Once amended) A method as defined in claim 1, wherein said dissolving [step] (a) comprises separately dissolving the A blocks and the B blocks into respective solutions.

3. (Once amended) A method as defined in claim 2, wherein said end-capping [step] (c) comprises separately end-capping the A blocks and the B blocks in the respective solutions.

4. (Once amended) A method as defined in claim 1, wherein said [steps] (a), (b), (c), and (d) are conducted in the absence of any halogenated solvent.

19. (Once amended) A method of making an energetic [composite binder] composition comprising:

(a) dissolving [the] A blocks and B blocks terminated with respective isocyanate-reactive groups at approximately [the] stoichiometric ratios [that are] intended to be present in the thermoplastic elastomer into solution comprising at least one non-halogenated solvent, the A blocks being crystalline [at temperatures] below about 75°C and derived from monomers comprising at least one member selected from the group consisting of oxetane derivatives and tetrahydrofuran derivatives, the B blocks being amorphous

[at temperatures] above about -20°C and derived from monomers comprising at least one member selected from the group consisting of oxetane and derivatives thereof, tetrahydrofuran and derivatives thereof, and oxirane and derivatives thereof;

- (b) drying the dissolved A blocks and B blocks of water by azeotropic distillation of the non-halogenated solvent;
- (c) end-capping the dried A blocks and the dried B blocks in the non-halogenated solvent by reacting the dried A blocks and the dried B blocks with at least one diisocyanate in which a first isocyanate moiety thereof is substantially more reactive with the terminal groups of the blocks as a second isocyanate moiety thereof, whereby the more reactive first isocyanate moiety is capable of reacting with the terminal groups of the blocks, leaving the less reactive second isocyanate moiety free and unreacted;
- (d) linking the end-capped A blocks and the end-capped B blocks together in the non-halogenated solvent with at least one linking compound comprising two isocyanate-reactive groups which are sufficiently sterically unhindered to react with the free and unreacted isocyanate moieties of the end-capped [polymers] blocks; and
- (e) blending the thermoplastic elastomer with about 50 wt% to about 95 wt% of at least one solid selected from the group consisting of fuel [material] particulates and oxidizer particulates.

20. (Once amended) A method as defined in claim 19, wherein said dissolving [step] (a) comprises separately dissolving the A blocks and the B blocks into respective solutions.

21. (Once amended) A method as defined in claim 20, wherein said end-capping [step] (c) comprises separately end-capping the A blocks and the B blocks in the respective solutions.

22. (Once amended) A method as defined in claim 19, wherein said [steps] (a), (b), (c), and (d) are conducted in the absence of any halogenated solvent.

30. (Once amended) A method of making a rocket motor propellant comprising making [a binder] an energetic composition as defined in claim 19.

31. (Once amended) A method of making a gun propellant comprising making [a binder] an energetic composition as defined in claim 19.

32. (Once amended) A method of making an explosive comprising making [a binder] an energetic composition as defined in claim 19.

33. (Once amended) A method of making a gasifier comprising making [a binder] an energetic composition as defined in claim 19.

AMENDED CLAIMS:

1. (Once amended) A method of preparing a thermoplastic elastomer comprising:

(a) dissolving A blocks and B blocks terminated with respective isocyanate-reactive groups at approximately stoichiometric ratios intended to be present in the thermoplastic elastomer into solution comprising at least one non-halogenated solvent, the A blocks being crystalline below about 75°C and derived from monomers comprising at least one member selected from the group consisting of oxetane derivatives and tetrahydrofuran derivatives, the B blocks being amorphous above about -20°C and derived from monomers comprising at least one member selected from the group consisting of oxetane and derivatives thereof, tetrahydrofuran and derivatives thereof, and oxirane and derivatives thereof;

(b) drying the dissolved A blocks and B blocks of water by azeotropic distillation of the non-halogenated solvent;

(c) end-capping the dried A blocks and the dried B blocks in the non-halogenated solvent by reacting the dried A blocks and the dried B blocks with at least one diisocyanate in which a first isocyanate moiety thereof is substantially more reactive with the terminal groups of the blocks as a second isocyanate moiety thereof, whereby the more reactive first isocyanate moiety is capable of reacting with the terminal groups of the blocks, leaving the less reactive second isocyanate moiety free and unreacted; and

(d) linking the end-capped A blocks and the end-capped B blocks together in the non-halogenated solvent with at least one linking compound comprising two isocyanate-reactive groups which are sufficiently sterically unhindered to react with the free and unreacted isocyanate moieties of the end-capped blocks.

2. (Once amended) A method as defined in claim 1, wherein said dissolving (a) comprises separately dissolving the A blocks and the B blocks into respective solutions.

3. (Once amended) A method as defined in claim 2, wherein said end-capping (c) comprises separately end-capping the A blocks and the B blocks in the respective solutions.

4. (Once amended) A method as defined in claim 1, wherein said (a), (b), (c), and (d) are conducted in the absence of any halogenated solvent.

19. (Once amended) A method of making an energetic composition comprising:

(a) dissolving A blocks and B blocks terminated with respective isocyanate-reactive groups at approximately stoichiometric ratios intended to be present in the thermoplastic elastomer into solution comprising at least one non-halogenated solvent, the A blocks being crystalline below about 75°C and derived from monomers comprising at least one member selected from the group consisting of oxetane derivatives and tetrahydrofuran derivatives, the B blocks being amorphous above about -20°C and derived from monomers comprising at least one member selected from the group consisting of oxetane and derivatives thereof, tetrahydrofuran and derivatives thereof, and oxirane and derivatives thereof;

(b) drying the dissolved A blocks and B blocks of water by

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(c) end-capping the dried A blocks and the dried B blocks in the non-halogenated solvent by reacting the dried A blocks and the dried B blocks with at least one diisocyanate in which a first isocyanate moiety thereof is substantially more reactive with the terminal groups of the blocks as a second isocyanate moiety thereof, whereby the more reactive first isocyanate moiety is capable of reacting with the terminal groups of the blocks, leaving the less reactive second isocyanate moiety free and unreacted;

(d) linking the end-capped A blocks and the end-capped B blocks together in the non-halogenated solvent with at least one linking compound comprising two isocyanate-reactive groups which are sufficiently sterically unhindered to react with the free and unreacted isocyanate moieties of the end-capped blocks; and

(e) blending the thermoplastic elastomer with about 50 wt% to about 95 wt% of at least one solid selected from the group consisting of fuel particulates and oxidizer particulates.

20. (Once amended) A method as defined in claim 19, wherein said dissolving (a) comprises separately dissolving the A blocks and the B blocks into respective solutions.

21. (Once amended) A method as defined in claim 20, wherein said end-capping (c) comprises separately end-capping the A blocks and the B blocks in the respective solutions.

22. (Once amended) A method as defined in claim 19, wherein said (a), (b), (c), and (d) are conducted in the absence of any halogenated solvent.

30. (Once amended) A method of making a rocket motor propellant comprising making an energetic composition as defined in claim 19.

31. (Once amended) A method of making a gun propellant comprising making an energetic composition as defined in claim 19.

32. (Once amended) A method of making an explosive comprising making an energetic composition as defined in claim 19.

33. (Once amended) A method of making a gasifier comprising making an energetic composition as defined in claim 19.

SYNTHESIS OF ENERGETIC THERMOPLASTIC ELASTOMERS
CONTAINING OLIGOMERIC URETHANE LINKAGES

5 Priority is claimed on United States Provisional Application 60/108,456 filed
on November 12, 1998, the complete disclosure of which is incorporated herein by
reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

10 This invention relates to energetic thermoplastic elastomers which are useful
as binders of high-energy compositions, such as propellants, especially rocket
propellants and gun propellants, explosive munitions, gas generants of vehicle
supplemental restraint systems, or the like, and to methods for synthesizing the same.

2. Description of the Related Art

15 Solid high-energy compositions, such as propellants, explosives, gasifiers, and
the like comprise solid particulates, such as fuel particulates and/or oxidizer
particulates, dispersed and immobilized throughout a polymeric binder matrix.

Conventional solid composite propellant binders utilize cross-linked
elastomers in which prepolymers are cross-linked by chemical curing agents. As
20 outlined in detail in U.S. Patent No. 4,361,526, there are important disadvantages to
using cross-linked elastomers as binders. Cross-linked elastomers must be cast within
a short period of time after addition of the curative, which time period is known as the
"pot life". Disposal of a cast, cross-linked propellant composition is difficult, and
usually is accomplished by burning, which poses environmental problems.
25 Furthermore, current state-of-the-art propellant compositions have serious problems
that include their use of nonenergetic binders which have lower performance and high
end-of-mix viscosities.

In view of the inherent disadvantages associated with the use of cross-linked
elastomeric polymers as binder materials, there has been considerable interest in
30 developing thermoplastic elastomers suitable as binders for solid, high energy
compositions. However, many thermoplastic elastomers fail to meet important
requirements expected of propellant formulations, particularly the requirement of

being processible below about 120°C, it being desirable that a thermoplastic elastomeric polymer for use as a binder in a high energy system have a melting temperature of between about 60°C and about 120°C. The melting temperature is desirably at least about 60°C because these compositions may be subject to somewhat elevated temperatures during storage and transport, and significant softening of the compositions at such elevated temperatures is unwanted. The setting of the melting temperature at not more than about 120°C is determined by the instability, at elevated temperatures, of many components which ordinarily go into the compositions, particularly oxidizer particulates and energetic plasticizers. Many thermoplastic elastomers exhibit high melt viscosities which preclude high solids loading and many show considerable creep and/or shrinkage after processing. Thermoplastic elastomers typically obtain their thermoplastic properties from segments that form glassy domains which may contribute to physical properties adverse to their use as binders. Crosslinkable thermoplastic elastomers are block copolymers with the property of forming physical cross-links at predetermined temperatures. One thermoplastic elastomer, e.g., Kraton, brand TPE, obtains this property by having the glass transition point of one component block above room temperature. At temperatures below 109°C, the glassy blocks of Kraton form glassy domains and thus physically cross-link the amorphous segments. The strength of these elastomers depends upon the degree of phase separation. Thus, it remains desirable to have controlled, but significant, immiscibility between the two types of blocks, which is a function of their chemical structure and molecular weight. On the other hand, as the blocks become more immiscible, the melt viscosity increases, thus having a deleterious effect on the processibility of the material.

Above-mentioned U.S. Patent No. 4,361,526 proposes a thermoplastic elastomeric binder which is a block copolymer of a diene and styrene, the styrene blocks providing a meltable crystal structure and the diene blocks imparting rubbery or elastomeric properties to the copolymer. The '526 patent states that this polymer is processed with a volatile organic solvent. Solvent processing is undesirable inasmuch as the dissolved composition cannot be cast in a conventional manner, e.g., into a rocket motor casing. Furthermore, solvent-based processing presents problems with respect to removal and recovery of solvent.

The preparation of energetic thermoplastic elastomers prepared from polyoxetane block copolymers has been proposed in U.S. Patent No. 4,483,978 to Manser and U.S. Patent No. 4,806,613 to Wardle ("the '613 patent"), the complete disclosures of which are incorporated herein by reference to the extent that these 5 disclosures are compatible with this invention. According to the latter, these materials overcome the disadvantages associated with conventional cross-linked elastomers such as limited pot-life, high end-of-mix viscosity, and scrap disposal problems.

The thermoplastic materials proposed by the '613 patent involve elastomers having both (A) and (B) blocks, each derived from cyclic ethers, such as oxetane and 10 oxetane derivatives and tetrahydrofuran (THF) and tetrahydrofuran derivatives. The monomer or combination of monomers of the (A) blocks are selected for providing a crystalline structure at usual ambient temperatures, such as below about 60°C, whereas the monomer or combination of monomers of the (B) blocks are selected to ensure an amorphous structure at usual ambient temperatures, such as above about 15 -20°C. Typical of these materials is the random block copolymer (poly(3-azidomethyl-3-methyloxetane)-poly(3,3-bis(azidomethyl)oxetane), also known as poly(AMMO/BAMO). These block copolymers have good energetic and mechanical properties. Additionally, the block copolymers can be processed without solvents to serve as binders in high performance, reduced vulnerability explosive, propellant, and 20 gas generant formulations. Advantageously, the block copolymers exhibit good compatibility with most materials used in such energetic formulations.

However, the block copolymers known in the art suffer from disadvantages that are a consequence of the short linking groups connecting the blocks. More 25 specifically, the short linking groups attribute relatively low softening temperatures to the copolymers. In tactical and other environments in which the binder is exposed to extreme environmental conditions, the binder should be capable of maintaining their structure integrities without creeping or slumping, and be characterized by a reasonable modulus at about 60°C or above. While the energetic binders disclosed in the '613 patent generally satisfy the processing requirements, they tend to soften 30 unacceptably at elevated temperatures that sometime are encountered in tactical and similar uses.

One proposed solution to addressing this problem and imparting desired high temperature attributes to the energetic binder is to select hard blocks, i.e., A blocks, having melting temperatures well above 60°C. However, the higher softening temperatures of such A blocks deleteriously affects the processability of the binder by 5 requiring higher and sometimes dangerous processing temperatures. Although solvents may be used to improve processability, the introduction of solvents limits the size of the articles that can be made and increases the complexity and costs of the process.

Another desired attribute of energetic binders is that the binders maintain 10 strength, toughness, and strain capability at extremely low temperatures, preferably below about -40°C. The polyethers used as the soft blocks, i.e., B blocks, in energetic thermoplastic elastomer binders tend to possess glass transition temperatures T_g in the range of -15°C to -30°C. Below these temperatures, the thermoplastic elastomer binders become brittle and lack sufficient toughness and strain capability. While 15 plasticization of the soft B block potentially could be a solution to lowering T_g of the thermoplastic elastomer, all attempts at plasticizing the B block have been found to require unacceptable plasticizer-to-polymer ratios, making the binder unusable at ambient and higher temperatures.

It would therefore be a significant advancement in the art to provide energetic 20 thermoplastic elastomer binders that are solid at room temperature and exhibit the excellent mechanical properties and processability of the materials disclosed in the '613 patent, while both possessing sufficiently high elevated temperature modulus and resistance to slump and creep while at the same time having a lower glass transition temperature or ability to be plasticized without adversely affecting high temperature 25 properties.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a thermoplastic elastomer that addresses the aforementioned problems associated with the related art and realizes the advancement expressed above.

In accordance with the principles of this invention, these and other objects are attained by the provision of an energetic thermoplastic elastomer binder that is in a solid state at room temperature and has A blocks and B blocks connected via linking groups derived from a difunctional urethane oligomer diol. The A blocks are

5 crystalline at temperatures below about 60°C and may be one or more polyether(s) derived from one or more monomers of oxetane derivatives and/or tetrahydrofuran derivatives. The B blocks are amorphous at temperatures above about -20°C and may be include one or more polyether(s) derived from one or more monomers of oxetane and its derivatives, tetrahydrofuran and its derivatives, and/or oxirane and its

10 derivatives. To effect linking, the A blocks and B blocks are capped with isocyanate moieties of diisocyanates. The isocyanate moieties of adjacent blocks are linked with an oligomer having two functional moieties that are reactive with an isocyanate moiety of the diisocyanate, hereinafter "a difunctional oligomer". The structure and length of the difunctional oligomer may be varied to tailor the properties of the

15 resulting thermoplastic elastomer.

It is also an object of this invention to provide a method for the preparation of the above-described energetic thermoplastic binder of this invention. In accordance with the principles of this invention, this and other objects are achieved by a method in which hydroxyl-terminated A blocks which are crystalline at temperatures below

20 about 60°C and hydroxyl-terminated B blocks which are amorphous at temperatures above about -20°C are end-capped with a diisocyanate. The diisocyanate preferably has one isocyanate moiety which is more reactive, preferably at least about five times as reactive, with the terminal hydroxyl group of each of the blocks than the other isocyanate moiety, whereby the more reactive isocyanate moiety tends to react with

25 the terminal-hydroxyl groups of the blocks, leaving the less reactive isocyanate moiety free and unreactive. The end-capped A blocks and the end-capped B blocks are mixed together at approximately the stoichiometric ratios that the blocks are intended to be present in the energetic thermoplastic elastomer. The mixture is reacted with a chain extender, i.e., an oligomeric linking compound having two

30 functional groups which are sufficiently unhindered to react with the free and unreacted isocyanate groups of the end-capped blocks. In this manner, the end-capped blocks are linked, but not cross-linked, to form a thermoplastic polymer.

It is still a further object of this invention to provide propellants, especially rocket propellants and gun propellants, explosives, gas generators, or the like containing the above-discussed energetic thermoplastic elastomer binder or made by procedures including the above-discussed method.

5 These and other objects, features, and advantages of the present invention will become apparent from the accompanying drawings and following detailed description which illustrate and explain, by way of example, the principles of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

10 The accompanying drawings are provided to facilitate an understanding of the principles of this invention. In such drawings, FIGS. 1 and 2 are graphs showing the properties of a thermoplastic elastomer prepared in accordance with an embodiment of this invention.

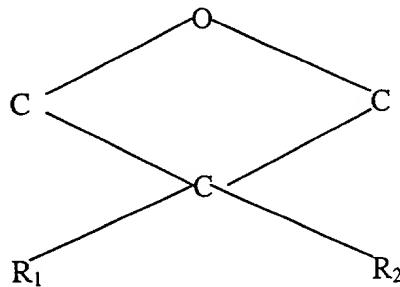
DETAILED DESCRIPTION OF THE INVENTION

15 The thermoplastic elastomer $(AB)_n$ polymers of this invention include A blocks which are crystalline at temperatures below about 60°C, preferably at temperatures below about 75°C, and B blocks which are amorphous at temperatures down to about -20°C. Each of the A and B blocks are polyethers derived from cyclic ethers. More specifically, the A blocks are derived from one or more monomers of 20 oxetane derivatives and/or monomers of one or more THF derivatives. The B blocks are derived from one or more monomers of oxetane and its derivatives, one or more monomers of THF and its derivatives, and/or one or more monomers of oxirane and its derivatives. The polymers melt at temperatures between about 60°C and about 120°C, and more preferably between about 75°C and about 100°C. The A and B 25 blocks are mutually miscible in the melt. Consequently, the melt viscosity of the block copolymer decreases rapidly as the temperature is raised above the melting point, whereby high energy formulations may include high solids content, e.g., up to about 95% by weight of solid particulates, and can be easily processed. The invention also includes other thermoplastic elastomer block structures, such as ABA tri-block

polymers and A_nB star polymers. Contributing to the miscibility of the A and B blocks is their similar chemical structure.

Oxetane monomer units that may be used in forming the A and B blocks of the present invention have the general formula:

5



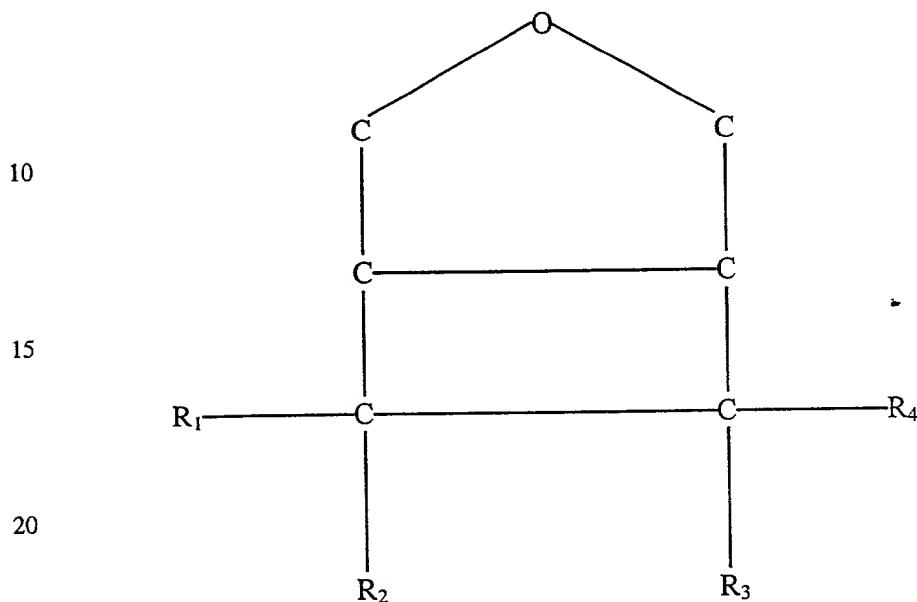
10 wherein the R_1 and R_2 groups are the same or different and are selected from moieties having the general formula: $-(CH_2)_nX$, where n is 0-10 and X is selected from the group consisting of -H, $-NO_2$, -CN, -Cl, -F, -O-alkyl, -OH, -I, $-ONO_2$, $-N(NO_2)$ -alkyl, $-C\equiv CH$, -Br, $-CH=CH$ (H or alkyl), $-CO_2$ (H or alkyl), $-N(H$ or alkyl) $_2$, $-O-(CH_2)_{1.5}-O-(CH_2)_{0.8}-CH_3$, and N_3 .

15 Examples of oxetane derivatives that may be used in forming the A blocks in accordance with this invention are generally symmetrically-substituted oxetanes including, but are not limited to, the following: BEMO (3,3-bis(ethoxymethyl)oxetane), BCMO (3,3-bis(chloromethyl)oxetane), BMMO (3,3-bis(methoxymethyl)oxetane), BFMO (3,3-bis(fluoromethyl)oxetane), BAOMO (3,3-bis(acetoxymethyl)oxetane), BHMO (3,3-bis(hydroxymethyl)oxetane), BMEMO (3,3-bis(methoxyethoxymethyl)oxetane), BIMO (3,3-bis(iodomethyl)oxetane), BNMO (3,3-bis(nitratomethyl)oxetane), BMNAMO (3,3-bis(methylnitraminomethyl)oxetane), and BAMO (3,3-bis(azidomethyl)oxetane).

20 Examples of oxetane derivatives that may be used in forming the B blocks in accordance with this invention are generally unsymmetrically-substituted oxetanes including, but are not limited to, the following: HMMO (3-hydroxymethyl-3-methyloxetane), OMMO (3-octoxymethyl-3-methyloxetane), CMMO (3-chloromethyl-3-methyloxetane), AMMO (3-azidomethyl-3-methyloxetane), IMMO

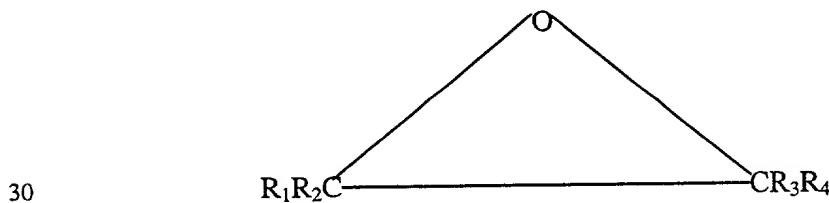
(3-iodomethyl-3-methyloxetane), PMMO (3-propynomethylmethyloxetane), NMMO (3-nitratomethyl-3-methyloxetane), and MNAMMO (3-methylnitraminomethyl-3-methyloxetane).

Tetrahydrofuran monomer units that may be used in forming the blocks of the present invention have the general formula:



wherein the R₁-R₄ groups are the same or different and are selected from moieties set forth above in connection with the description of suitable oxetane derivatives.

Oxirane monomer units used in forming the B blocks of the present invention have the general formula:



wherein R_1 and R_3 are independently selected from hydrogen and methyl, and R_2 and R_4 are independently selected from hydrogen, alkyl containing from 1 to 10 carbon atoms, chloroalkyl and bromoalkyl containing 1 to 2 carbon atoms, and nitratoalkyl, nitratoalkoxyalkyl, nitroalkyl, nitroalkoxyalkyl, azidoalkyl, azidoalkoxyalkyl,

fluoronitroalkyl, and fluoronitroalkyoxyalkyl containing 1 to 5 carbon atoms provided that at least one of R₁ to R₄ is not hydrogen.

Examples of energetic oxiranes that may be used in forming the B blocks in accordance with this invention include, but are not limited to glycidyl azide polymers 5 (C₃H₅N₃O) (GAP), especially difunctional GAP, and poly(glycidyl nitrate) (C₃H₅NO₄) (PGN). These polymers have a glass transition temperature below about -20°C and are amorphous at temperatures above -20°C.

Forming thermoplastic elastomers in accordance with the invention involves 10 (1) formation of at least one polyether-derived homopolymer, copolymer, or terpolymer serving as the A blocks and crystalline in nature with a relatively elevated melting point, i.e., between about 60°C and about 120°C, preferably near 80°C and (2) formation of at least one polyether-derived homopolymer, copolymer, or terpolymer serving as the B blocks and amorphous in structure with a glass transition temperature (T_g) below about -20°C.

15 The selection of the A block may be made based on the properties desired for the intended application of the thermoplastic elastomer. Examples of preferred crystalline A blocks include blocks possessing high energy density, such as those formed from BAMO and/or BMNAMO monomers. Melting temperature and ether oxygen content are additional factors that may be taken into consideration in selecting 20 the monomers.

The properties of the block polymer depends upon the molecular weights of the individual blocks. Typically the A blocks have number average molecular 25 weights ranging from about 3000 to about 8000, whereas the B blocks have number average molecular weights ranging from about 3000 to about 15,000. The weight ratio of A blocks to B blocks is preferably between about 15:85 to about 40:60. The preferred sizes of the A and B blocks for any particular binder application may be empirically determined.

The thermoplastic elastomers of this invention preferably are in a solid state at room temperature, have a weight average molecular weight of at least 40,000, more 30 preferably at least 60,000, still more preferably at least 80,000, and a number average

molecular weight of at least 10,000, more preferably at least 12,000, still more preferably at least 15,000.

Thermoplastic elastomers produced in accordance with the present invention may be admixed with other components of a high energy formulation, such as a 5 propellant formulation. The binder system, in addition to the thermoplastic elastomers, may optionally contain one or more plasticizers for improving the resistance of the thermoplastic elastomer to hardening at low temperatures, which may be included at a plasticizer-to-thermoplastic elastomer weight ratio of up to about 1:1. Suitable high energy plasticizers include glycidyl azide polymer (GAP), 10 nitroglycerine, butanetriol trinitrate (TTTN), alkyl nitratomethyl nitramines, trimethylolethane trinitrate (TMETN), diethylene glycol dinitrate, triethylene glycol dinitrate (TEGDN), bis(dinitropropylacetal/-bis(dinitropropyl)formal (BDNPA/F), and mixtures thereof. Inert plasticizers can also be used. Representative inert 15 plasticizers include, by way of example, dioctyladipate (DOA), isodecylperlargonate (IDP), dioctylphthalate (DOP), dioctylmaleate (DOM), dibutylphthalate (DBP), oleyl nitrile, triacetin, and combinations thereof. The binder system may also contain a minor amount of a wetting agent or lubricant that enables higher solids loading.

The solids content of the high energy composition generally ranges from about 50 wt% to about 95 wt%, higher solids loading generally being preferred so long as 20 such loading is consistent with structural integrity. The solids include fuel material particles and powders (collectively referred to herein as particulates), such as particulate aluminum, and/or oxidizer particulates. Representative fuels include aluminum, magnesium, boron, and beryllium. Representative oxidizers and co-oxidizers include ammonium perchlorate; hydroxylammonium nitrate (HAN); 25 ammonium dinitramide (ADN); hydrazinium nitroformate; ammonium nitrate; nitramines such as cyclotetramethylene tetranitramine (HMX) and cyclotrimethylene trinitramine (RDX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane or 2,4,6,8,10,12- 30 hexanitrohexaazaisowurtzitane (CL-20 or HNTW), and/or 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (TEX), and any combination thereof. In addition, the high energy composition may include minor amounts of

additional components known in the art, such as bonding agents, burn rate modifiers, ballistic modifiers (e.g., lead), etc.

The thermoplastic elastomer may be mixed with the solids and other components of high energy formulation at temperatures above its melting 5 temperature. Blending may be done in conventional mixing apparatus. Because of the low viscosities of the molten polymer, no solvents are required for blending or other processing, such as extrusion.

An important advantage of having a binder which is meltable is that the elastomer from an outdated device containing can be melted down and reused. At the 10 time of such remelting, the binder might be reformulated, e.g., by addition of additional fuel or oxidizer particulates. Accordingly, the thermoplastic elastomer provides for its eventual recycle, as opposed to the burning required for disposal of cross-linked compositions. Because the "pot life" of the thermoplastic propellant exceeds that which would reasonably be required of a propellant or explosive 15 formulation, if any problems develop during casting, the process can be delayed as long as is reasonably necessary, merely by maintaining the formulation in a molten state.

The oxetane homopolymer blocks may be formed according to the cationic polymerization technique taught by Manser in U.S. Patent No. 4,393,199, the 20 complete disclosure of which is incorporated herein by reference. The oxirane homopolymer blocks may be formed according to the technique taught in U.S. Patent No. 5,120,827, the complete disclosure of which is incorporated herein by reference. The technique employs an adduct of a substance such as a diol, e.g., 1,4-butane diol (BDO), and a catalyst for cationic polymerization, e.g., BF_3 -etherate. This adduct 25 forms with the oxetane monomer an initiating species which undergoes chain extension until n moles of monomer have been incorporated in the molecule, n being the ratio of monomers to adduct present. By adjusting the ratio of monomers to adduct present, the average molecular weight of the polymer which forms may be adjusted. If two or more monomers are present, incorporation of the monomers will 30 be generally random but may depend upon the relative reactivities of the monomers in the polymerization reaction.

Another suitable catalyst system includes co-catalytically effective quantities of one or more triethoxonium salts and one or more alcohols, as disclosed in U.S. Application No. 08/233,219, the complete disclosure of which is incorporated herein by reference to the extent that the disclosure is compatible with this invention.

5 Examples of triethoxonium salts include triethoxonium hexafluorophosphate, triethoxonium hexafluoroantimonate, and triethoxonium tetrafluoroborate.

It is understood that although the isocyanate-reactive terminal functional groups of the blocks are referred to herein as being hydroxyl groups, the isocyanate-reactive functional groups may also be amines, amides, and/or carboxyl groups.

10 The crystalline polyoxetane A blocks and amorphous B blocks, i.e., the respective prepolymers, are each end-capped together or separately with one or more diisocyanates. The end-capped A and B blocks are mixed together and joined by a linking compound which has a pair of isocyanate-reactive functionalities that are sufficiently unhindered to allow them to react with the free isocyanate moieties of the 15 end-capped copolymers and thereby join the blocks together.

Oxetane, THF, and oxirane polymer blocks normally have terminal isocyanate-reactive (e.g., hydroxyl) functions which are end-capped with the diisocyanates in accordance with the invention. Preferably, one of the isocyanate moieties of the end-capping diisocyanate is substantially more reactive with the 20 terminal-hydroxyl moieties of the polymer blocks than the other isocyanate moiety. One of the problems with linking these types of polymer blocks is that substituted oxetane-derived hydroxyl end groups units have neopentyl structures, whereby the terminal primary hydroxyl moieties are substantially hindered and therefore less reactive. The blocks derived from oxirane derivatives are secondary alcohols, making 25 their hydroxyl groups less reactive than the primary hydroxyl groups of the oxetane derived A blocks. The diisocyanate preferably is selected so that one of the isocyanate groups is capable of reacting with a hydroxyl-group of the polymer blocks while the other isocyanate moiety remains free and unreacted. Diisocyanates are preferably used because isocyanates of higher functionality would result in 30 undesirable levels of cross-linking. The different reactivities of the isocyanate moieties is desirable to ensure that substantial chain extension through linking of like blocks does not occur. Thus, for purposes of this invention, one isocyanate moiety of

the diisocyanate should preferably be approximately five times more reactive with terminal hydroxyl groups of oxetane and oxirane blocks than the other group.

Preferably one isocyanate moiety is at least about ten times more reactive than the other.

5 One diisocyanate which is especially useful for purposes of the invention is 2,4-toluene diisocyanate (TDI) in which the isocyanate moiety in the 4-position is substantially more reactive with hindered terminal hydroxyl moieties than the isocyanate moiety in the 2-position. Isophorone diisocyanate (IPDI) is suitable for some applications, though less so than TDI. Examples of diisocyanates which have
10 not worked well include diphenylmethylene diisocyanate (MDI) and hexamethylene diisocyanate (HDI).

In the end-capping reaction, the diisocyanate is used at an approximately stoichiometric molar amount relative to terminal hydroxyl groups on the polymer chain. Thus, if the polymer chain has a pair of terminal hydroxyl groups,
15 approximately two molar equivalents, e.g., 1.75-2.2 molar equivalents of diisocyanate are used. In the ideal reaction, all of the more reactive isocyanate moieties would react with terminal hydroxyl groups, leaving all of the less reactive isocyanate moieties free. Practically, not all of the diisocyanate reacts in this manner, and some chain extension does occur. Thus, the end-capping reaction may be maximized for
20 particular polymer chains by some adjustment in the relative molar ratios of polymer block and diisocyanate.

In one variant embodiment, the A blocks and B blocks are reacted separately with the diisocyanate, so that there is no competition of the blocks for diisocyanate molecules and each separate end-capping reaction may be carried to substantial completion. The diisocyanate may react more rapidly with one block than the other, but this difference can be compensated for by a longer reaction time with the slower reacting block. The reactivity of the terminal hydroxyl groups varies according to steric factors and also according to side-chain moieties. Energetic oxetanes, for example, generally have side-chain moieties that are electron-withdrawing, making
25 their terminal hydroxyl groups less reactive. Once end-capped with diisocyanate, the reactivities of the polymers for linking purposes is essentially dependent only upon the reactivity of the free isocyanate, not on the chemical makeup of the polymer chain
30

itself. Thus end-capped (A) blocks are substantially as reactive as end-capped (B) blocks. The end-capping of the oxirane blocks in this manner overcomes the problems associated with linking of oxirane-derived blocks which have secondary hydroxyl groups.

5 The end-capping reaction and linking reaction are carried out in a suitable solvent, e.g., one which dissolves the polymer and does not react with the free isocyanate moieties. In a preferred embodiment, the solvent is non-halogenated. Although insubstantial amounts of halogenated solvent may be present, the solution is preferably completely free of any halogenated solvent. The non-halogenated solvent 10 should not react in the urethane reaction (i.e., do not interfere with the end capping catalyst, such as dibutyl tin dilaurate, or the linking catalyst) and forms an azeotrope with water. The solvent or solvents selected preferably are capable of dissolving more than 25% by weight of the blocks (based on total weight of the solvents and blocks) into solution, more preferably at least 35% by weight into solution, and still 15 more preferably 50% by weight into solution. Representative solvents include cyclic ethers such as tetrahydrofuran (THF) and 1,4-dioxane; non-cyclic ethers such as ethylene glycol dimethyl ether; ketones such as methyl ethyl ketone (MEK); and esters such as ethyl acetate. Of these, THF is preferred because of its excellent solubility characteristics.

20 In a preferred embodiment, the solvent forms an azeotrope with water. In this preferred embodiment, after the blocks are dissolved in excess non-halogenated solvent, the solution may be dried by azeotropic distillation of the solvent, and optionally further concentrated, e.g., via distillation, in the solution to increase the volumetric loading and reaction rate. The blocks then may be end-capped, separately 25 or together, and linked in the same or a different non-halogenated solvent. By distilling off excess solvent to remove water, subsequent reaction with a diisocyanate may proceed without significant interference from competing reactions between the isocyanate moieties and water. Additionally, the solution remains homogeneous and further distillation serves to concentrate the polymer solution, producing higher 30 reaction rates and requiring less reactor capacity. The reaction rates may be improved by conducting the end-capping reaction at elevated temperatures, such as 30°C to 80°C, more preferably 40°C to 60°C. The process may be conducted by a batch or

continuous method. For example, the prepolymer and catalyst may be continuously fed through a mixer/extruder into which is injected a diisocyanate and a diol at appropriate rates and positions so that urethane linking occurs within the extruder and energetic thermoplastic elastomer is continuously produced for processing.

5 Suitable catalysts for promoting the end-capping reaction include, as a preferred class, organic tin compounds with at least one and preferably two labile groups, such as chloride or acetate, bound directly to the tin. Suitable tin catalyst include diphenyl tin dichloride, dibutyl tin dichloride, dibutyl tin dilaurate, dibutyl tin diacetate. Tertiary amine catalysts may also be used.

10 The oligomeric linking compound is one which has two functional groups which are sufficiently unhindered to react with the free isocyanate moieties on the end-capped blocks so as to link A blocks to B blocks, A blocks to A blocks, and B blocks to B blocks via a urethane reaction. Preferred functional groups are hydroxyl groups, although amine, amide, and carboxyl groups, and mixtures thereof also react 15 in a urethane reaction. Primary functional groups are preferred.

20 An oligomeric glycol containing urethane moieties is preferably used to react the free isocyanate moieties on the end-capped blocks. The oligomeric glycol may be prepared from a mixture of one or more diisocyanates and an excess amount of one or more diols. The diisocyanate(s) and diol(s) selected and the ratio of these reagents 25 may be varied to tailor the properties of the thermoplastic elastomer. The diol to diisocyanate molar ratio is preferably selected to be between 5:1 to 5:4, more preferably about 2:1, to maintain acceptable processing temperatures, obtain adequate linking of the isocyanate-capped prepolymers, and improve the thermomechanical properties of the final thermoplastic elastomer. A suitable urethane reaction catalyst 30 promotes the reaction between the diisocyanate(s) and diol(s) to form oligomers. The catalysts discussed above in connection with the linking of the A and B blocks are suitable for this purpose. Representative diols that may be selected for preparing the difunctional oligomer include, by way of example, unbranched aliphatic diols having 2 to 7 carbon atoms, such as ethylene glycol, propylene glycol, butylene glycol; and 35 cycloaliphatic diols such as 1,4-cyclohexanedimethanol, and any combination thereof. Representative diisocyanates for preparing the difunctional oligomer include, by way of example, aliphatic diisocyanates such as hexane diisocyanate, and aryl

diisocyanates such as methylene-bis(4-phenyl isocyanate), phenylene diisocyanate, toluene diisocyanate, and xylylene diisocyanate, and any combination thereof.

Preferably, the difunctional oligomer has a number average molecular weight M_n of from 350 to 900.

5 As in the end-capping reaction, some solvent is preferably used, as is a catalyst, such as described above. Conveniently, the reaction mixtures of the A blocks and B blocks may be mixed together without prior separation of the blocks from their respective end-capping reaction mixtures. The linking compound can be added directly to this mixture of A and B blocks. The catalyst is thereby already
10 present when the linking compound is added.

The linking compound is added in an amount such that the total number of linking-compound functional groups approximately equals the total number of free isocyanate groups of the end-capped polymer blocks. Thus, to provide an $(AB)_n$ polymer with multiple blocks in each chain, the linking compound to polymer block
15 molar ratio is in the range of 0.9-1.1, e.g., 1.0. Accordingly, optimal molar ratios of blocks and linking chemicals may have to be empirically determined.

In the end-capping and block linking steps, the reaction can be followed with NMR and IR. With NMR, the urethane-forming reaction can be followed through the methylene groups on the polymer adjacent to the terminal hydroxyl groups. With IR,
20 the change from isocyanate to urethane can be directly followed.

Synthesis of polyoxetanes is described in U.S. Patent Nos. 4,483,978 and 4,806,613, the complete disclosures of which are incorporated herein by reference to the extent such disclosures are compatible with this invention.

The invention will now be described in greater detail by way of the following
25 examples, which are not to be construed as being exhaustive as to the scope of this invention.

As referred to herein, "dry" means that less than 1 wt% water was present.

For the following experiments, poly(azidomethyloxirane) was supplied by 3M Speciality Chemicals of St. Paul, MN (Lot L-12564). Unless otherwise specified, all other materials were obtained from Aldrich of Milwaukee, WI.

EXAMPLE 1 (poly(3,3-bis(azidomethyl)oxetane))

5 A 5 liter jacketed flask equipped with a mechanical stirrer was charged with 600 grams of tribromoneopentylalcohol (AmeriBrom, Inc. of New York), 1200 ml of toluene, and 6 grams of tetrabutylammonium bromide. The mixture was cooled to 12°C and 193 grams of sodium hydroxide was added dropwise as a 40 wt% solution keeping the temperature at 12°C. After 36 hours the reaction mixture was washed
10 with water until the pH was less than 9 to obtain the crude product which was distilled to obtain 3,3-bis(bromomethyl)oxetane at 65% yield.

A 5 liter jacketed flask equipped with a mechanical stirrer was charged with 1450 grams of the 3,3-bis(bromomethyl)oxetane and 1720 ml of toluene. The mixture was stirred and heated to 60°C before 1600 ml of water, 14.7 grams of
15 tetrabutylammonium bromide, and 862 grams of sodium azide were added. After 24 hours, the reaction mixture was cooled to room temperature and washed three times with 2000 ml of water. The toluene and water were removed from the organic layer by distillation to give pure 3,3-bis(azidomethyl)oxetane at 85% yield.

Under an argon atmosphere, 14.94 grams of butane diol was added to a flame
20 dried 5 liter round-bottomed flask charged with 1340 ml of dry methylene chloride. To this mixture, 11.77 grams of borontrifluoride-etherate was added and the reaction was allowed to proceed for one hour at room temperature. The reactor was then cooled to -10°C and 937.78 grams of the 3,3-bis(azidomethyl)oxetane was added. The solution was allowed to come to room temperature and left to react for three days.
25 The reaction was then quenched by the addition of 50 ml of saturated brine solution. The organic phase was separated off and washed with 100 ml of 10 wt% sodium bicarbonate solution before the solvent was removed on a rotovapor. The resulting liquid was then poured into 5 liters of methanol to precipitate the polymer, which was filtered from the solution and dried under vacuum at 30°C.

30 EXAMPLE 2 (poly(3-azidomethyl-3-methyloxetane))

A 5 liter jacketed flask equipped with a mechanical stirrer was charged with

1062 grams of sodium azide, 1972 ml of water, and 2450 grams of 3-bromomethyl-3-methyloxetane (supplied by AmeriBrom, Inc. of New York). This mixture was brought to reflux with vigorous mixing. After 48 hours the mixture was cooled to room temperature. The organic layer was separated off and washed three times with 5 1000 ml of water before being dried over molecular sieves to yield pure 3-azidomethyl-3-methyloxetane at 85% yield.

Under an argon atmosphere, 14.94 grams of butane diol was added to a flame dried 5 liter round-bottomed flask charged with 1.340 ml of dry methylene chloride. To this mixture, 11.77 grams of borontrifluoride-etherate was added and the reaction 10 was allowed to proceed for one hour at room temperature. The reactor was then cooled to -10°C and 937.78 grams of the 3-azidomethyl-3-methyloxetane was added. The solution was allowed to come to room temperature and left to react for three days. The reaction was then quenched by the addition of 50 ml of saturated brine solution. The organic phase was separated off and washed with 100 ml of 10 wt% sodium 15 bicarbonate solution before the solvent was removed on a rotovapor. The resulting liquid was then poured into 5 liters of methanol to precipitate the polymer, which was filtered from the solution and dried under vacuum at 30°C.

EXAMPLE 3 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) linked with a urethane oligomer)

20 In a 25 ml round bottom flask, a urethane oligomer was prepared by dissolving 2.70 grams of toluene-2,4-diisocyanate in 5 ml tetrahydrofuran and adding to the solution 0.2 grams of dibutyltin dilaurate followed by 2.80 grams of butane-1,4-diol. This reaction mixture was stirred for 1 hour at room temperature.

25 In a separate 500 ml round bottom flask, 68.34 grams of dry dihydroxyl poly(3-azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3356 and 34.54 grams of dry poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3235 were dissolved in 400 ml of dry methylene chloride. The solution was concentrated and dried by evaporation of the tetrahydrofuran under reduced pressure via a rotovapor until 100 grams of the solvent remained. To this solution, 2.5 grams 30 of dibutyltin dilaurate and 5.61 grams of toluene-2,4-diisocyanate were added while stirring with a magnetic stirrer at ambient temperature and pressure. After one hour, the urethane oligomer was added to this solution, causing the solution to become

steadily more viscous. After an additional four hours, the solution was diluted with methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product with the following properties:

5 $E^{1.0}$ (psi) = 1122

ϵ_m (%) = 303

ϵ_f (failure) (%) = 327

σ_m (psi) = 362

σ_m (corrected) (psi) = 1504

10 ShoreA = 63

($E^{1.0}$ represents Young's Modulus. ϵ_m and ϵ_f , respectively representing maximum measured strain and calculated failure strain, and σ_m and σ_m (corrected), respectively representing measured maximum stress and calculated corrected maximum stress, were measured using an INSTRON model 1225. The crosshead speed was 0.6 inches per minute. Measurements were made at room temperature using 20 mm x 4 mm dumbbell samples. ShoreA representing hardness was measured on a Shore Conveloader at room temperature.)

EXAMPLE 4 (Random block copolymer of poly(azidomethyloxirane) and poly(3,3-bis(azidomethyl)oxetane))

20 In a 25 ml round bottom flask, a urethane oligomer was prepared by dissolving 1.55 grams of toluene-2,4-diisocyanate in 4 ml tetrahydrofuran and adding to the solution 0.1 ml of dibutyltin dilaurate followed by 1.60 grams of butane-1,4-diol. This reaction mixture was stirred for 1 hour at room temperature.

25 In a separate 250 ml round bottom flask, 17.94 grams of dry difunctional poly(azidomethyloxirane) with a hydroxyl equivalent weight of 1174 and 6.63 grams of dry poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 2390 were dissolved in 100 ml of dry tetrahydrofuran. The solution was concentrated and dried by evaporation of the tetrahydrofuran under reduced pressure via a rotovapor

until 20 grams of the solvent remained. To this solution, 75 ml of dibutyltin dilaurate and 3.097 grams of toluene-2,4-diisocyanate were added while stirring with a magnetic stirrer at ambient temperature and pressure. After one hour, the urethane oligomer was added to this solution, causing the solution to become steadily more 5 viscous. After 20 minutes, the solution was too viscous to stir and was diluted with 20 ml of dry tetrahydrofuran and allowed to react for a further 20 minutes before being poured into methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product with the properties shown in FIGS. 1 and 2 10 and set forth below:

Mn = 26240

Mw = 175500

Mw/Mn = 6.69

15 Molecular weight distribution was determined by gel permeation chromatography using polystyrene standards, with the results shown in FIG. 1. The GPC trace in FIG. 1 demonstrates that the prepolymers were linked to produce a copolymer having a higher molecular weight and dispersivity than the homopolymer blocks. The DMA trace in FIG. 2 shows the melt transition of random block (BAMO-GAP)_n at 75-80°C with a material modulus reducing only slowly before this 20 point.

EXAMPLES 5-7 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) linked with a urethane oligomer)

In a 500 ml round bottom flask, 45 grams of difunctional poly(3-azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3125 and 15 grams of 25 poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3152 were dissolved in 300 ml of tetrahydrofuran. The solution was concentrated and dried by evaporation of the tetrahydrofuran or a rotovapor until a solution with 90 grams of solvent remained. To this solution 0.6 grams of dibutyltin dichloride and 3.34 grams of toluene-2,4-diisocyanate was added and the mixture allowed to react for 3 hours to 30 end-cap the prepolymer.

For Example 5, 0.22 grams of butanediol was added to one quarter of the isocyanate end-capped prepolymer mixture. The reaction was allowed to continue for 14 hours before it was precipitated with methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with 5 fresh methanol (1:5 volume ratio) to give a rubbery granular product.

For Example 6, a urethane oligomer was derived from a mixture of 2 ml of tetrahydrofuran, 0.42 grams of toluene-2,4-diisocyanate, 0.43 grams of butane-1,4-diol, and 0.1 grams of dibutyltin dichloride, which were allowed to react for one 10 hours. The urethane oligomer was then added to one quarter of the isocyanate end-capped prepolymer mixture and allowed to react for 14 hours before it was precipitated with methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product.

For Example 7, a urethane oligomer was derived from a mixture of 2 ml of 15 tetrahydrofuran, 0.83 grams of toluene-2,4-diisocyanate, 0.65 grams of butane-1,4-diol, and 0.1 grams of dibutyltin dichloride, which were allowed to react for one hours. The urethane oligomer was then added to one quarter of the isocyanate end-capped prepolymer mixture and allowed to react for 14 hours before it was 20 precipitated with methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product.

TABLE 1

	Example 5	Example 6	Example 7
diol:diisocyanate molar ratio	1:0	2:1	3:2
Mn	11440	12340	13240
Mw	134800	142000	122600
Mw/Mn	11.78	11.51	9.26
E ^{1.0}	520	669	823
ε _m (%)	311	897	536
ε _f (failure) (%)	372	1082	562
σ _m (psi)	153	345	300
σ _m (corrected) (psi)	678	3575	2381
ShoreA	49	60	65

EXAMPLE 8 AND COMPARATIVE EXAMPLE A

In a 50 ml beaker, 10 grams of random block poly(3-azidomethyl-3-methyloxetane)polymer(3,3-bis(azidomethyl)oxetane)) prepared with either an oligomeric linkage derived from butane-1,4-diol and toluene-2,4-diisocyanate (Example 8) or butane-1,4,-diol (Comparative Example A) were dissolved in 10 ml of tetrahydrofuran. To this solution was added 1.25 grams of triethyleneglycol dinitrate and 1.25 grams of butyl nitrotoethylnitramine. The solvent was removed by evaporation in a vacuum over at 60°C. The plasticized polymer was then melted at 90°C, poured onto a flat TEFLON plate and allowed to solidify at room temperature for 48 hours before being cut into 20 mm x 4 mm dumbbell samples and subjected to testing:

TABLE 2

	Example 8	Comparative Example A
diol:diisocyanate molar ratio	2:1	1:0
wt % energetic plasticizer	20	20
$E^{1.0}$ (psi)	174	Plasticized polymer too soft to make samples
ε_m (%)	126	
ε_f (corrected) (%)	139	
σ_m (psi)	62	
σ_m (corrected) (psi)	141	
ShoreA	28	

The foregoing detailed description of the preferred embodiments of the invention has been provided for the purpose of explaining the principles of the invention and its practical application, thereby enabling others skilled in the art to understand the invention for various embodiments and with various modifications as are suited to the particular use contemplated. The foregoing detailed description is not intended to be exhaustive or to limit the invention to the precise embodiments disclosed. Modifications and equivalents will be apparent to practitioners skilled in this art and are encompassed within the spirit and scope of the appended claims.

WHAT IS CLAIMED IS:

1. A thermoplastic elastomer having A blocks and B blocks and being present in a substantially solid state suitable for use as a binder for at least one of a propellant, explosive, and gasifier, the thermoplastic elastomer being formulated from 5 a composition comprising, as constituents:
 - A blocks terminated with isocyanate-reactive groups derived from monomers comprising at least one member selected from the group consisting of oxetane derivatives and tetrahydrofuran derivatives, the A blocks being crystalline at temperatures below about 75°C;
 - 10 B blocks terminated with isocyanate-reactive groups derived from monomers comprising at least one member selected from the group consisting of oxetane and derivatives thereof, tetrahydrofuran and derivatives thereof, and oxirane and derivatives thereof, the B blocks being amorphous at temperatures above about -20°C; and
 - 15 linking groups derived from at least one diisocyanate for end-capping the A blocks and the B blocks and at least one difunctional oligomer comprising two functional groups which are reactive with isocyanate moieties of the diisocyanate.
2. A thermoplastic elastomer as defined in claim 1, wherein:
 - the diisocyanate contains a first isocyanate moiety which is at least five times 20 more reactive with the terminal groups of the blocks than a second isocyanate moiety thereof, whereby the more reactive first isocyanate moiety is capable of reacting with and end capping the terminal groups of the blocks, leaving the less reactive second isocyanate moiety free and unreacted; and
 - 25 the difunctional oligomer has two isocyanate-reactive hydroxyl groups which are sufficiently sterically unhindered to be reactive with the free and unreacted second isocyanate moieties of the end-capped blocks.
3. A thermoplastic elastomer as defined in claim 2, wherein the diisocyanate comprises toluene diisocyanate.
4. A thermoplastic elastomer as defined in claim 1, wherein the A blocks 30 are crystalline at temperatures below about 60°C.

5. A thermoplastic elastomer as defined in claim 1, wherein the difunctional oligomer comprises a reaction product of at least one diol and at least one diisocyanate, the diol being selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, and 1,4-cyclohexanedimethanol, and any 5 combination thereof.

6. A thermoplastic elastomer as defined in claim 1, wherein the difunctional oligomer comprises a reaction product of at least one diol and at least one diisocyanate, the diisocyanate being selected from the group consisting of hexane diisocyanate, methylene-bis(4-phenyl isocyanate), phenylene diisocyanate, toluene 10 diisocyanate, and xylylene diisocyanate, and any combination thereof.

7. A thermoplastic elastomer as defined in claim 1, wherein the thermoplastic elastomer has a weight average molecular weight of at least 40,000 and a number average molecular weight of at least 10,000.

8. A thermoplastic elastomer as defined in claim 1, wherein the 15 thermoplastic elastomer has a weight average molecular weight of at least 60,000 and a number average molecular weight of at least 12,000.

9. A thermoplastic elastomer as defined in claim 1, wherein the thermoplastic elastomer has a weight average molecular weight of at least 80,000 and a number average molecular weight of at least 15,000.

20 10. A thermoplastic elastomer as defined in claim 1, wherein a weight ratio of A to B blocks is between about 15:85 to about 40:60.

11. A thermoplastic elastomer as defined in claim 1, wherein the isocyanate-reactive terminal groups of the A and B blocks are hydroxyl groups.

12. A binder comprising:
25 about 50 wt% to about 95 wt% of at least one solid selected from the group consisting of fuel material particulates and oxidizer particulates; and
at least one thermoplastic elastomer having A blocks and B blocks and being present in a substantially solid state to immobilize the particulates, the thermoplastic elastomer being formed from a composition comprising, as constituents:

A blocks terminated with isocyanate-reactive groups derived from monomers comprising at least one member selected from the group consisting of oxetane derivatives and tetrahydrofuran derivatives, the A blocks being crystalline at temperatures below about 75°C;

5 hydroxyl-terminated B blocks terminated with isocyanate-reactive groups derived from monomers comprising at least one member selected from the group consisting of oxetane and derivatives thereof, tetrahydrofuran and derivatives thereof, and oxirane and derivatives thereof, the B blocks being amorphous at temperatures above about -20°C; and

10 linking groups derived from at least one diisocyanate for end-capping the blocks and at least one difunctional oligomer comprising two functional groups which are reactive with isocyanate moieties of the diisocyanate.

13. A binder according to claim 12, wherein:

 the diisocyanate contains a first isocyanate moiety which is at least five times 15 more reactive with the terminal groups of the blocks than a second isocyanate moiety thereof, whereby the more reactive first isocyanate moiety is capable of reacting with and end capping the terminal-groups of the blocks, leaving the less reactive second isocyanate moiety free and unreacted; and

 the difunctional oligomer has two isocyanate-reactive hydroxyl groups which 20 are sufficiently sterically unhindered to be reactive with the free and unreacted second isocyanate moieties of the end-capped blocks.

14. A binder as defined in claim 12, wherein the A blocks are crystalline at temperatures below about 60°C.

15. A binder as defined in claim 12, wherein the difunctional oligomer 25 comprises a reaction product of at least one diol and at least one diisocyanate, the diol being selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, and 1,4-cyclohexanedimethanol, and any combination thereof.

16. A binder as defined in claim 12, wherein the difunctional oligomer comprises a reaction product of at least one diol and at least one diisocyanate, the 30 diisocyanate being selected from the group consisting of hexane diisocyanate,

methylene-bis(4-phenyl isocyanate), phenylene diisocyanate, toluene diisocyanate, and xylylene diisocyanate, and any combination thereof.

17. A binder as defined in claim 12, wherein the solid is at least one member selected from the group consisting of aluminum particulates, ammonium perchlorate, and ammonium nitrate.

18. A binder as defined in claim 12, further comprising at least one member selected from the group consisting of cyclotetramethylene tetranitramine (HMX), cyclotrimethylene trinitramine (RDX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (CL-20), and 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (TEX).

19. A binder as defined in claim 12, further comprising at least one energetic plasticizer selected from the group consisting of glycidyl azide polymer (GAP), nitroglycerine, butanetriol trinitrate (BTTN), alkyl nitratomethyl nitramines, trimethylolethane trinitrate (TMETN), diethylene glycol dinitrate, triethylene glycol dinitrate, and bis(dinitropropylacetal/-bis(dinitropropyl)formal (BDNPA/F).

20. A binder as defined in claim 12, wherein the isocyanate-reactive terminal groups of the A and B blocks are hydroxyl groups.

21. A rocket motor propellant comprising the binder of claim 12.

22. A gun propellant comprising the binder of claim 12.

20 23. An explosive comprising the binder of claim 12.

24. A gasifier comprising the binder of claim 12.

25. A method of preparing a thermoplastic elastomer having A blocks which are crystalline at temperatures below about 75°C and the B blocks which are amorphous at temperatures above about -20°C, the method comprising:
25 providing A blocks and B blocks at approximately the stoichiometric ratios that are intended to be present in the thermoplastic elastomer, the A blocks being terminated with isocyanate-reactive functional groups, crystalline at temperatures below about 75°C, and derived from monomers comprising at least one member

selected from the group consisting of oxetane derivatives and tetrahydrofuran derivatives, the B blocks being terminated with isocyanate-reactive functional groups, amorphous at temperatures above about -20°C, and derived from monomers comprising at least one member selected from the group consisting of oxetane and 5 derivatives thereof, tetrahydrofuran and derivatives thereof, and oxirane and derivatives thereof;

end-capping the A blocks and the B blocks by reacting the A blocks and B blocks with at least one diisocyanate in which a first isocyanate moiety thereof is at least about five times more reactive with the terminal groups of the blocks than a 10 second isocyanate moiety thereof, whereby the more first reactive isocyanate moiety is capable of reacting with the terminal groups of the blocks, leaving the less reactive second isocyanate moiety free and unreacted; and

linking the end-capped A blocks and the end-capped B blocks together with a difunctional oligomer comprising two isocyanate-reactive groups which are 15 sufficiently sterically unhindered to react with the free and unreacted second isocyanate moieties of the end-capped polymers.

26. A method as defined in claim 25, wherein the diisocyanate comprises toluene diisocyanate.

27. A method as defined in claim 25, wherein the A blocks are crystalline 20 at temperatures below about 60°C.

28. A method as defined in claim 25, further comprising preparing the difunctional oligomer by reacting at least one diol and at least one diisocyanate, the diol being selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, and 1,4-cyclohexanedimethanol, and any combination thereof.

25 29. A method as defined in claim 25, further comprising preparing the difunctional oligomer by reacting at least one diol and at least one diisocyanate, the diisocyanate being selected from the group consisting of hexane diisocyanate, 20 methylene-bis(4-phenyl isocyanate), phenylene diisocyanate, toluene diisocyanate, and xylylene diisocyanate, and any combination thereof.

30. A method as defined in claim 25, wherein the isocyanate-reactive terminal groups of the A and B blocks are hydroxyl groups.

ABSTRACT OF THE DISCLOSURE

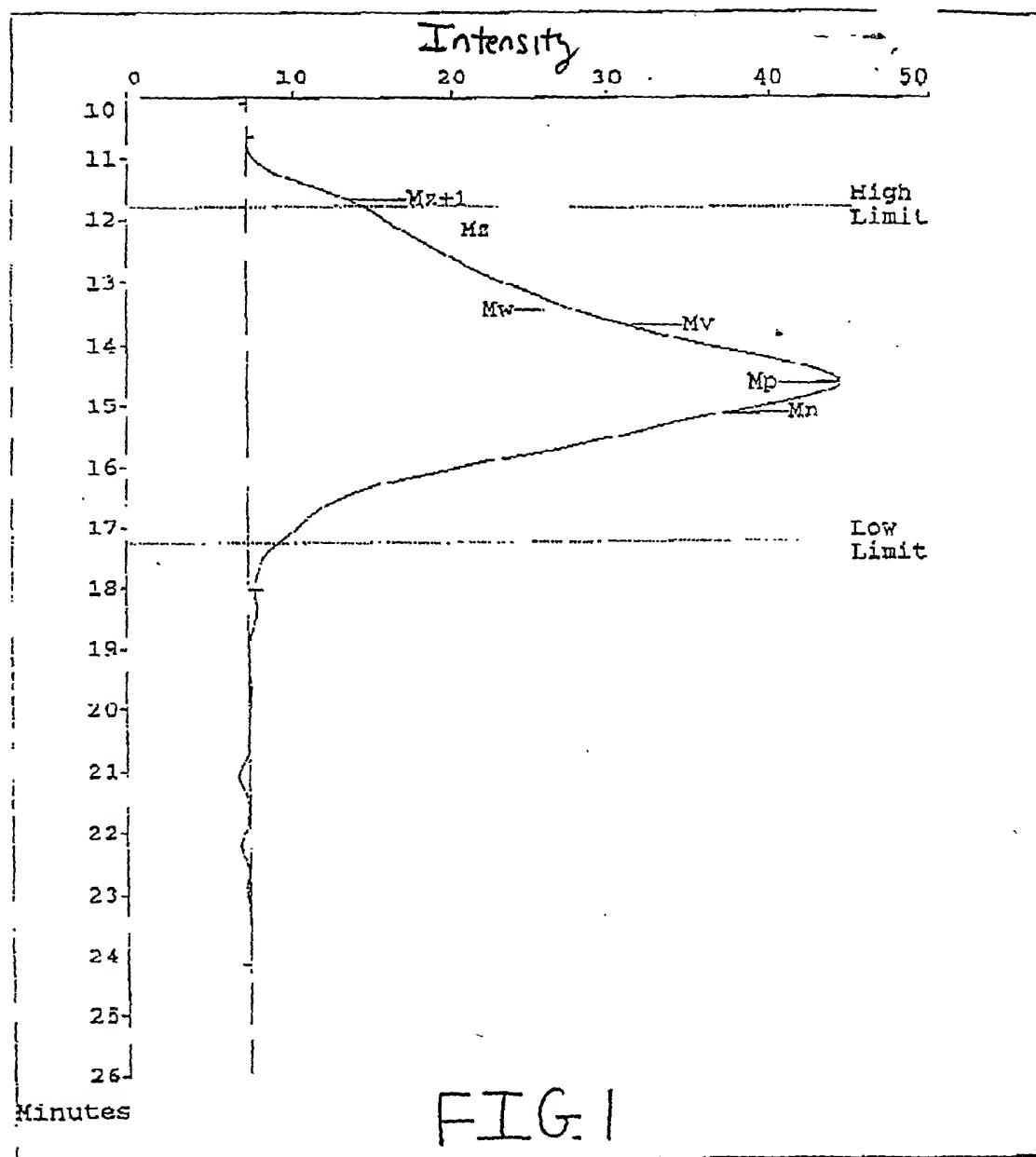
This thermoplastic elastomer is present in a substantially solid state suitable for use as a binder for a propellant, explosive, and/or gas generant of a supplemental restraint system. The thermoplastic elastomer is formed from a composition including

5 A blocks which are crystalline at temperatures below about 75°C and B blocks which are amorphous at temperatures above about -20°C. The A blocks are derived from oxetane derivatives and/or tetrahydrofuran derivatives. The B blocks are derived from oxetanes, tetrahydrofuran, oxiranes, and derivatives thereof. The A and B blocks are end-capped with at least one diisocyanate and linked with at least one

10 difunctional oligomer having two functional groups which are reactive with free and unreacted isocyanate moieties of the diisocyanate.

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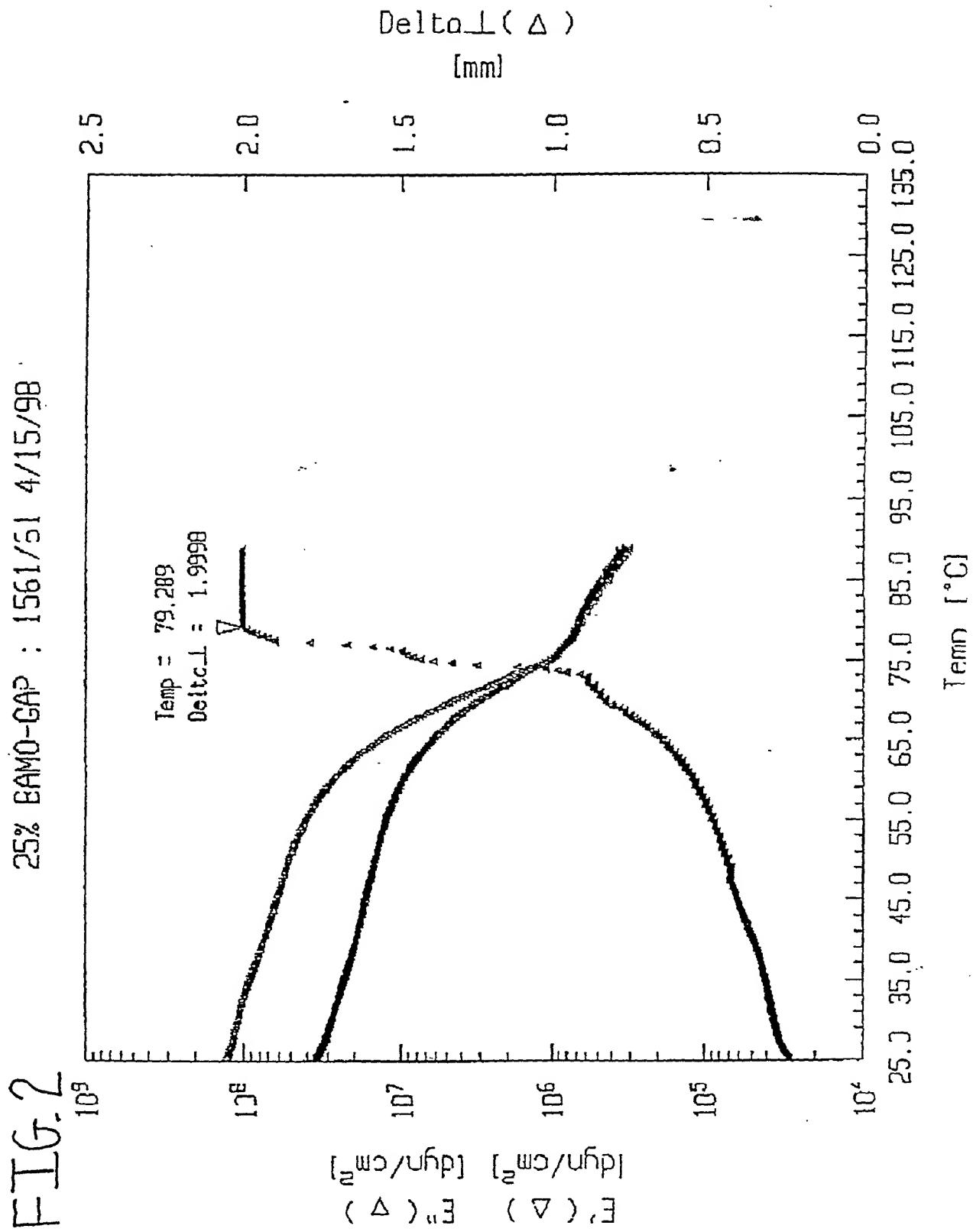
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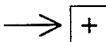
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**DECLARATION FOR UTILITY OR
DESIGN
PATENT APPLICATION
(37 CFR 1.63)**

Declaration Submitted OR Declaration Submitted after Initial Filing (surcharge (37 CFR 1.16 (e)) required)

Attorney Docket Number		1082-033
First Named Inventor		Sanderson, et al.
COMPLETE IF KNOWN		
Application Number	/	
Filing Date		
Group Art Unit		
Examiner Name		

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Method for the Synthesis of Energetic Thermoplastic Elastomers in Non-Halogenated Solvents

the specification of which *(Title of the Invention)*

is attached hereto

OR

was filed on (MM/DD/YYYY) **11/09/1999** as United States Application Number or PCT International

Application Number **PCT/US99/24013** and was amended on (MM/DD/YYYY) **06/09/00** (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims as amended specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY) Country	Priority Not Claimed	Certified Copy Attached?	
				YES	NO
PCT/US99/24013	PCT	11/09/1999	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
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Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto

I hereby claim the benefit under 35 U.S.C. 119(e) of any United States provisional application(s) listed below

ApplicationNumber(s)	Filing Date (MM/DD/YYYY)	<input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto
60/108,455	11/12/1998	

[Page 1 of 2]

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Given Name <u>Andrew J.</u>		Family Name <u>SANDERSON</u> or Surname			
Inventor's Signature <u>ML</u>				Date <u>2 May '01</u>	
Residence: City <u>North Ogden</u>	State <u>Utah</u>	Country <u>U.S.A.</u>	Citizenship <u>U.K.</u>		
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NAME OF SECOND INVENTOR:		<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name <u>Wayne W.</u>		Family Name <u>EDWARDS</u> or Surname			
Inventor's Signature <u>Wayne Edwards</u>				Date <u>5-2-01</u>	
Residence: City <u>Tremonton</u>	State <u>Utah</u>	Country <u>U.S.A.</u>	Citizenship <u>U.S.</u>		
Mailing Address <u>600 S., 610 West</u>	<u>VT.</u>				
Mailing Address					
City <u>Tremonton</u>	State <u>Utah</u>	ZIP <u>84337</u>	Country <u>U.S.A.</u>		
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Application Number	Not Yet Assigned
Filing Date	Herewith
First Named Inventor	Sanderson, et al.
Group Art Unit	Not Yet Assigned
Examiner Name	Not Yet Assigned
Attorney Docket Number	1082-033

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Name	Registration Number
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David S. Taylor	39,045

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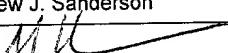
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Applicant.

Assignee of record of the entire interest. See 37 CFR 3.71.

Certificate under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96).

SIGNATURE of Applicant or Assignee of Record

Name	Andrew J. Sanderson
Signature	
Date	2 May 01

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Application Number	Not Yet Assigned
Filing Date	Herewith
First Named Inventor	Sanderson, et al.
Group Art Unit	Not Yet Assigned
Examiner Name	Not Yet Assigned
Attorney Docket Number	1082-033

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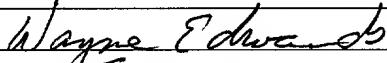
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SIGNATURE of Applicant or Assignee of Record

Name	Wayne W. Edwards
Signature	
Date	5-2-01

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required.
Submit multiple forms if more than one signature is required, see below*.

*Total of 2 forms are submitted.

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